Thermodenuder-Aerodyne Aerosol Mass Spectrometer System: Lab Characterization and Initial Field Deployment Results

J. ALEX HUFFMAN, and Jose-Luis Jimenez, Dept. of Chem. and CIRES, Univ. of Colorado at Boulder
Paul J. Ziemann, Dept. of Environmental Sciences, Univ. of California, Riverside
John T. Jayne, Timothy Onasch, and Doug R. Worsnop, Aerodyne Research Inc., MA.

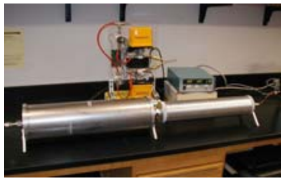
Introduction

A thermodenuder (TD) has been designed and built based on the design of Wehner *et al* (2002). The instrument is comprised of a heated tube, followed by a charcoal diffusion denuder, and is designed to evaporate particle-phase species at a given temperature, which is then stepped over the course of an experiment. The TD was coupled as the front end of an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) in order to achieve volatility separation before mass-spectral analysis.

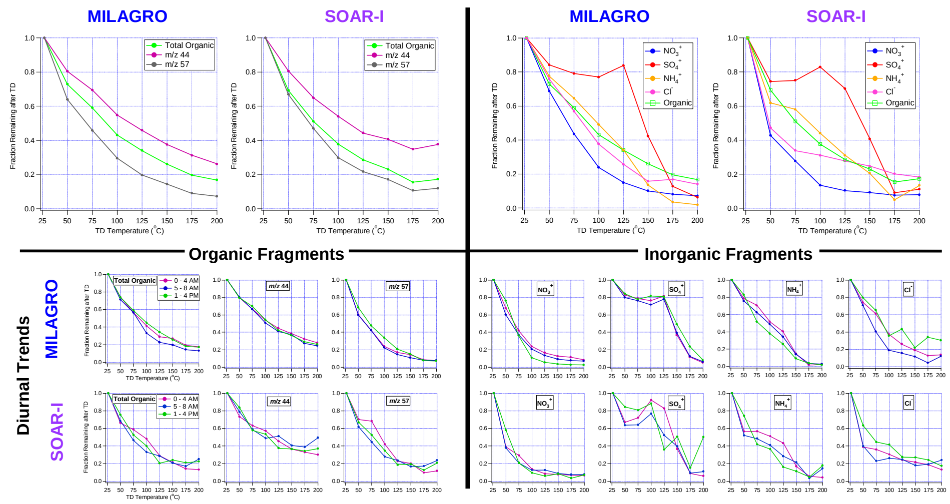
After lab characterization, the thermal denuder was deployed on four field campaigns. Example results from two experiments are shown to illustrate both the operation of the instrument, and to highlight the beginning of new information being gained. The two campaigns highlighted here are:

SOAR-I took place in Riverside, CA during July and August of 2005. (See 1B3, 8G12).
MILAGRO took place in Mexico City during March of 2006. (See 6B1, 6G19, 7H15)

Wehner, B., S. Philippin, and A. Wiedensholer, Design and Calibration of a Thermodenuder with an Improved Heating Unit to Measure the Size-Dependent Volatile Fraction of Aerosol Particles, *Journal of Aerosol Science*, *33*(7), 1087-1093, 2002.



Comparison of MILAGRO and SOAR-I



The above plots show a comparison between volatility data taken in the SOAR-I and MILAGRO field campaigns. The top four plots show an average of each respective campaign, separating the organic and inorganic species for comparison. Each "thermogram" plot shows the fraction of the aerosol mass remaining at a given temperature (with respect to the ambient data immediately closest in time). The bottom section shows individual species in each plot. Three time periods were averaged, each for the entire sampling campaign: 0 – 4 AM (late night), 5 – 8 AM (morning rush hour), and 1 – 4 PM (mid-afternoon). Plots from the two campaigns are plotted above one another for easy comparison. Note that while *m/z* 57 can be considered a marker for HOA, the nominal mass also contains contribution from $C_3H_5O^+$ (see high resolution plot below). A small portion of the initial drop from ambient temperature (here 27 °C) to 50 °C is due to particles losses due to diffusion and thermophoresis. This effect is still being quantified.

Conclusions

TECHNIQUE:

- A thermodenuder (TD) has been designed, built, and tested based on the Wehner *et al.* (2002) design.
- The TD was coupled with a HR-ToF-AMS to produce novel datasets of volatility-MS in real time.
- The novel fast temperature cycling enables continuous volatility analysis at a number of temperatures.

FIELD CAMPAIGNS:

- Sulfate is less volatile than other species, as expected
- Nitrate is typically the most volatile species
- Ammonium and organics fall in between sulfate and nitrate
- Ammonium and nitrate were more volatile in in SOAR-I than MILAGRO, and chloride was much more so. This may be due to chemical differences or matrix effects.
- Overall, most species do not show diurnal variability of volatility.
- m/z 44 shows considerably lower volatility than m/z 57. Similar results for other oxygenated (OOA) and hydrocarbon-like (HOA) markers.

ACKNOWLEDGEMENTS

The authors are grateful for funding from: DOE Grant DE-FG02-05ER63981 (BER), EPA Star Grant R831080, NASA ESS Fellowship NGTS-30516, NSF Career Grant ATM-0449815.

Initial Characterization

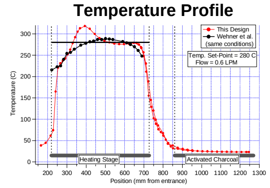
Lab characterization was performed to evaluate the design compared to the initial Wehner *et al* (2002). paper. The temperature profile, and passing efficiency are shown below, with data from Wehner *et al* (2002) plotted as well.

Lab characterization of the instrument is ongoing. Particles losses due to diffusion and thermophoresis are large only for very small particles below the AMS transmission window. Artifacts due to re-condensation are also possible at high concentrations, and we are investigating them. The plots below show that the performance is reasonably similar to those published by the initial design.

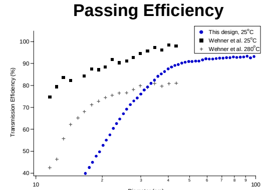
The flow rate is typically set to 0.6 lpm, which leaves a residence time of approximately 9 s within the heated region.

A valve system was designed and built to switch between ambient and TD. This allows rapid cycling for improved time and temperature resolution.

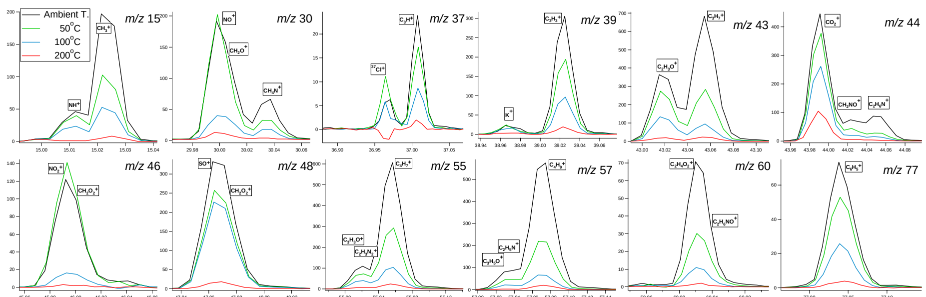
Temperature Profile

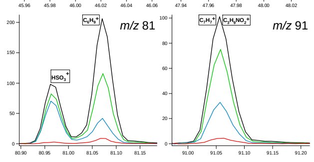


Passing Efficiency



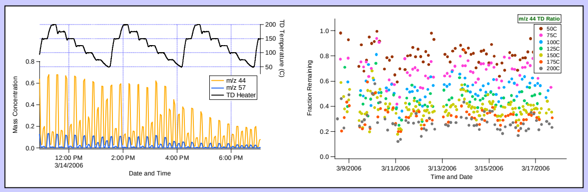
High-Resolution Spectra as a Function of Temperature





HR Spectra

The plots above show high resolution mass spectra at 14 nominal masses. Tags indicating fragments present in significant amounts are shown. The four colors span the range of temperatures at which the aerosol was conditioned. Ambient temperature (TD bypassed) and three temperatures of the TD are shown. All of the above plots were taken from individual AMS runs during the MILAGRO-2006 field campaign at approximately 6AM on 3/16/06. This was during a fairly typical weekday morning of moderate overall aerosol concentration and significant rush hour exhaust concentration. These plots are shown to show the ability of the coupled system to determine volatility of individual fragments.



Rapid Data Collection

A significant improvement in this thermodenuder design is that temperature cycling can take place on a rapid basis. In typical field campaign use, the TD will run at 25 °C steps from 50°C to 200°C, over the course of two hours and forty minutes. This is achieved by spending ten minutes in ambient mode, and then ten minutes at some temperature. As the valves switch back to ambient state, the temperature is changed so as to give it time to settle before sampling through the thermodenuder again. The plot on the left shows the TD temperature cycling on the top, and the way the AMS data initially looks as the valves switch the ambient aerosol stream through the TD, and directly into the AMS. One can see a typical stair-step pattern within the TD points as the temperature is ramped. The plot to the right shows the time series of the fraction of *m/z* 44 remaining versus time, with each nominal temperature shown in a different color.

Montana FLAME Study

The thermodenuder-AMS couple was also used in the FLAME study at the Missoula Fire Sciences Lab in Missoula, MT during the first week of June, 2006. This study provided an opportunity to demonstrate the novel rapid temperature cycling of the instrument. Over the course of a two hour burn we were able to cycle between heated and ambient aerosol in excess of 25 times to gain much improved sampling time and temperature resolution. The plots below show both the varied biomass output of different woods, and example output from this analysis.